

AN INFRARED STUDY OF THE OXIDATION
OF ORGANIC COMPOUNDS

by

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INTRODUCTION

The problem of determining specifically the atomic configuration of chemical molecules has long been one of a time consuming nature to the organic chemist. In many cases, of which isomerism is an example, it was nearly impossible to determine chemically the structural constitution of a compound. The study of characteristic infrared absorption spectra which began in the late 19th century revealed an entirely new avenue for investigating molecular structure.

Some of the earliest investigation of infrared spectra was carried out by Abney and Festing in England in 1881 (1). These investigators found selective absorption bands similarly situated in the spectra of a number of compounds containing the methyl group. A short time later Julius (2) published the results of the examination of a large number of compounds containing the methyl group. Julius noted absorption bands in the regions of 3.45 microns and 8 to 9 microns which he believed to be due to the presence of the methyl group. In 1897 Nichols (3) developed a prism spectrometer more adapted to infrared studies. The conventional NaCl prism was used as the dispersive medium and the intensity of the radiation was measured by a radiometer. This spectrometer, with a few minor modifications, was utilized by an early American investigator, W. W. Coblentz (4). Coblentz began his investigations by studying the spectrum of iodine. This effort was extended to include the compounds of

fuchsine and cyanine (5). These materials were known to be chemically similar and, from the similar absorption spectra at 6.5 microns and 8.2 microns, Goblentz inferred that the two were of similar physical structure. In 1904 Goblentz published the results of the investigation of about 100 compounds each containing the hydroxyl group (6). The absorption spectra of each contained a strong band at 2.95 microns which he concluded to be characteristic of the OH configuration. This particular piece of work indicates the advance in technique accomplished during the period of the late 19th century to 1904 in the accuracy with which the OH band was identified. One of the earliest recording spectrometers was used by Weniger in 1910 (7) to study the effect of isomerism, mode of linkage and the effect of polymerism. He concluded, as did Goblentz, that the spectra of similar compounds must be similar. In 1911 data from infrared line spectra were collected by H. M. Randall (8). The region covered was from 0.75 micron to 3 microns and the information accumulated was found useful in verifying the Ritz combination principal. Advance in method and theory continued with the work of such investigators as Schaefer and Schubert (9), Lecompte (10) and Ellis (11). One of the earliest studies of complex molecules was made by Ross (12) when he investigated the spectra of pyrones. By 1928 the study of infrared had progressed to the point where texts on the subject appeared. The theory of band spectra has been treated extensively in texts by Ta You Wu (13) and Herzberg (14).

The application of infrared analysis to industrial problems began about 1936. Since that time its use has been expanded greatly; largely due to the fact that commercially built recording spectrometers were made available by such companies as Baird Associates, The Beckman Company and the Perkin Elmer Corporation. At present industrial application is quite widespread being of particular utility to the chemical and petroleum industry in the control of distillation and fractionation processes and in the determination of the purity of various products. Contributions to the knowledge of the specific physical configuration of many complex molecules have recently been made by infrared analysis of chemical reactions. A general discussion of these various techniques is given in the text "Infrared Determination of Organic Structures" (15) published in 1949. Included in this book is a catalogue of the wavelengths attributed to vibrations of various functional groups. Some of these assignments have been empirically determined but most are based on theoretical analysis. This catalogue was used in the Kansas State College Infrared Laboratory for the assignment of groups to absorption bands found in various oxidation reactions. Another assemblage of information very useful to the infrared spectroscopist is the file of spectra compiled by the laboratories affiliated with the American Petroleum Institute. Such spectra find application mainly in the identification of compounds by their characteristic infrared absorption spectra.

THE ORIGIN OF INFRARED ABSORPTION SPECTRA

The theory of molecular structure indicates that all molecules are composed of a group of atoms bound together by forces as yet not completely explained. At a temperature of other than absolute zero, the atoms perform oscillations about their equilibrium positions at frequencies of from 10^{13} to 10^{14} cycles per second; these frequencies are of the same order of magnitude as the frequencies of vibration of the electromagnetic radiation in the infrared region. The infrared region extends from approximately 1 micron to 25 microns. Some of the molecular vibrations give rise to a change in the dipole moment of the molecule and as is predicted from classical considerations (16) absorb all or part of the radiation which may be incident upon it if the frequency of the incident radiation is exactly that of the vibrations of the atoms. The number and nature of these vibrations depend upon the complexity of the molecule but it may be shown (14) that any molecular vibration may be resolved into the vector sum of a number of simple harmonic vibrations which are, by definition, normal modes of vibration. A linear molecule composed of n atoms would have $3n-5$ normal modes while a non-linear molecule would have $3n-6$ (14). In addition to vibrational motion, a molecular configuration of atoms has certain rotational motions associated with it. The effect of these rotational energies is to change each of the vibrational frequencies into a group of frequencies which are so close together that, except under high

dispersion, they appear as a band. This effect is of little consequence in the analysis of complex molecules.

From the above reasoning it might be thought that the normal modes of vibration for any molecule could be calculated. For simple molecules this is true and a number of calculations have been made by Herzberg (14), and others, from theoretical considerations alone and later verified experimentally. However, for complex molecules, the mathematical treatment becomes prohibitively complicated. Much information concerning vibrational motions in complex molecules has been obtained entirely by empirical considerations. It has been determined, with good theoretical justification, that given atomic groups such as C-H, O-H, C-C etc. execute certain vibrational motions due to the forces existing between these atoms and that these vibrations are changed very little by forces exerted by the other atoms with which the group may be associated in various molecules (13, 14). Experimental verification of this was found in observing the spectra of a number of compounds and noting regions having similar absorption bands. By determining chemically what group or groups were common to all the compounds, the frequencies of vibration of a given group might be inferred. An example of the spectral correlation which exists between similar molecular configurations is shown in Fig. 2. Regions of similarity are noted at 3.3 microns to 3.5 microns, the C-H stretching vibration region, and in the C-H bending region from 6.8 to 20 microns.

EXPLANATION OF PLATE I

Fig. 1. Typical record as taken from the Perkin Elmer infrared spectrometer.

Fig. 2. Infrared spectra of related compounds.

PLATE I

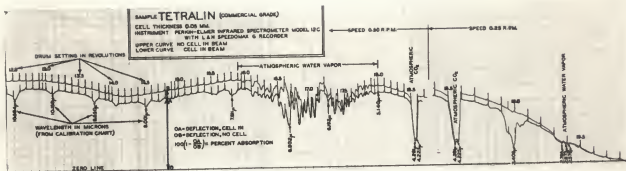
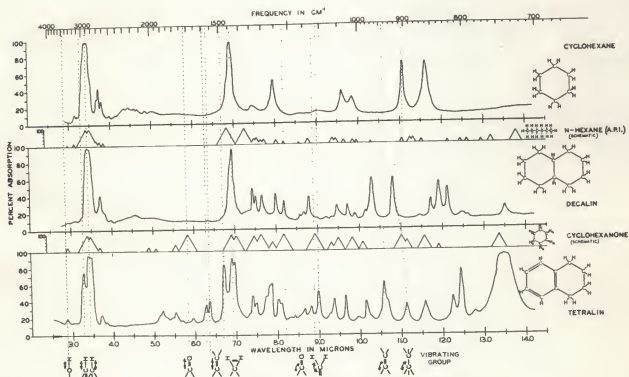


Fig. 1



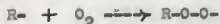
INFRARED SPECTRA OF RELATED COMPOUNDS

SHOWING FREQUENCIES CHARACTERISTIC OF CERTAIN ATOMIC GROUPS

Fig. 2

STATEMENT OF PROBLEM

The specific mechanism of the autoxidation of various ketones is a question which has never been completely explained, in fact little work has been reported in this field. It has been considered that autoxidation of most ketones was an extremely slow process in the absence of suitable catalysts. At a recent symposium on oxidation in England a number of investigators presented evidence that the oxidation of organic compounds was initiated by the formation of a free radical from the parent molecule by the extraction of a neutral hydrogen atom (19). This change has been explained, at least partially, by the dehydrogenation theory of Wisland (20). The reaction with molecular oxygen is believed to proceed as follows:



the final free radical of the parent molecule then occupies the position of the initial radical and the reaction proceeds in a chain reaction. In most cases, the hydroperoxide of the substance is unstable and, with the further addition of oxygen, decomposes into more stable molecules. These intermediate and final products apparently act as catalyzing agents in the formation of the initial free radicals and as a result the absorption rate of oxygen increases rapidly in the intermediate stage after the concentrations of the various compounds become significant.

The termination stage is probably the most complex feature of the autoxidation. Termination of individual chains probably commences soon after oxidation initiation, but the termination stage is that in which the oxygen absorption rate slows and much of the starting material has been consumed. The final reaction product must then be a heterogeneous mixture of different oxygenated compounds including peroxides, alcohols, ketones, aldehydes, acids, etc.

The problem in the present instance was to apply both chemical and infrared spectroscopic analysis to typical ketones during the progress of their oxidation and to attempt to correlate the data thus collected with the theory discussed above. It was possible to chemically separate the end products which formed upon oxidation and also to determine by chemical means the concentrations of the several products at different points during the oxidation period (17).

Infrared spectral analysis offered a means whereby the formation or decomposition of various functional groups could be determined. This was possible because of the characteristic selective absorption which is found in the infrared region for many groups of which O-H bending and stretching vibrations and C=O bending and stretching vibrations are examples. In this laboratory the precise wavelength of particular absorption bands was determined empirically. An example of this determination was in the determination of the position of the O-H stretching band when associated with a hydroperoxide molecule and when associated with an iso-butyric acid molecule. The differentiation was accomplished by the preparation of standard

mixtures in di-iso-propyl ketone of the hydroperoxide of this ketone and another mixture of iso-butyric acid in the ketone; these two compounds were isolated chemically from the oxidized samples of the ketone and thus were known to be products of the decomposition. It was possible under the high resolution of the LiF prism to resolve the spectra of these two solutions in the 3 micron (OH stretching) region into two bands; one at 3.1 microns due to the OH associated with the acid and one at 2.95 microns due to the hydroperoxide OH. In standard solutions of di-iso-propyl ketone and its final oxidation products other bands were identified in other regions of the spectrum. The location of new absorption bands produced in early oxidations carried out for the purpose of development of technique is indicated in Table 1. The assignment of corresponding functional groups to the bands was made from the catalogue compiled by Randall et al. (15). This information from the various spectral regions proved useful in making concentration determinations for the various products throughout the oxidation reactions.

Table 1. New or shifted frequencies produced in the infrared spectra of ketones by oxidation.

Frequencies in cm^{-1}		:	Tentative assignment	
Ketone		:		
Di-n-propyl	Di-iso-propyl	:	Type	Compound
3450	3450		O-H stretch	Hydroperoxide
3220 } <u>a</u>	3220 } <u>a</u>		O-H stretch	Acid
1780 } <u>a</u>			C=O stretch	Acid
1600 } <u>a</u>			C=O stretch	Ketone
1400 <u>b</u>	1370 <u>b</u>		O-H bend	Acid and hydroperoxide
1250 } <u>a</u>	1250 } <u>a</u>		skeletal	Ketone
1160 } <u>a</u>	1160 } <u>a</u>		skeletal	Acid and hydroperoxide
1075	1030		C-(OH) stretching	Acid
940	940		skeletal	
	910		skeletal	
	877		skeletal	
850 } <u>a</u>	850 } <u>a</u>		C-(OOH)	Hydroperoxide
775 } <u>a</u>	775 } <u>a</u>		skeletal	Acid

a indicates a general increase in absorption in region enclosed in brackets.

b this frequency is somewhat masked by strong absorption of the parent compound.

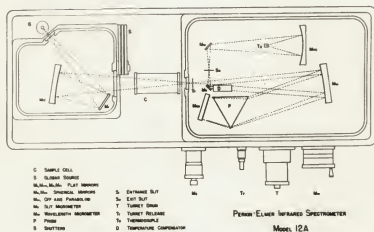
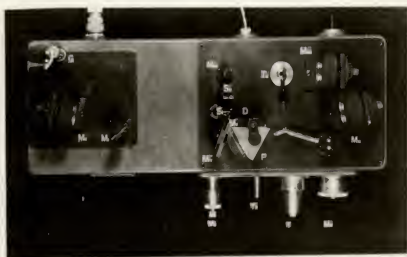
EXPERIMENTAL PROCEDURE

The oxidation and chemical analysis of the group of ketones considered was conducted by Leo W. Patton (17). Oxidation of samples was carried out in a four foot tower consisting of a pyrex tube upon which was wound a chromel ribbon heating element. The material to be oxidized was placed in the tower and molecular oxygen was bubbled through it. Provision was made for withdrawing samples from the center of the column at any time during the oxidation period and samples were withdrawn at various times. Computations by chemical means were made of the concentrations of the decomposition products in units of millimoles per gram sample for each sample withdrawn. The infrared spectrum was recorded for each sample with a Perkin Elmer Infrared Spectrometer Mod. 12C, Plate III. Prisms for the instrument were of the demountable type making possible the utilization of prisms composed of materials of different dispersion and absorption properties for different regions of the spectrum. Three types of prisms are available in the laboratory. LiF was used for the region from 1.5 to 5.5 microns giving relatively high dispersion in this range. NaCl was used for scanning the complete spectrum from 2.5 to 15 microns with relatively large dispersion from 6 to 15 microns. The KBr prism was not used for this work but is useful in extending the range to 25 microns. A rotating Littrow mirror, M_{Ly} , mounted adjacent to the prism and driven by a micrometer screw causes the spectrum to pass across a defining slit from which it is focused on a sensitive

EXPLANATION OF PLATE III

Photograph and schematic optical diagram of spectrometer
source and monochromometer housings.

PLATE III



thermopile, T_0 . Small thermopile voltages are amplified by a factor of 10^3 by a linear DC amplifier and fed into a Leeds Northrup Speedomax Recorder. The deflection of the recorder pen is a linear function of the intensity of the radiation falling on the thermopile. Figure 1 is a typical record obtained by making two scanning runs of the entire spectrum using the NaCl prism. The top record is obtained with no sample in the beam; it shows the background spectrum (atmospheric H_2O vapor, CO_2 etc.). The bottom record is the spectrum of the sample in question (tetralin in the example). By subtracting the sample deflection from the background deflection and dividing by background deflection the percent of absorption and from this the optical density, due to the sample only, may be obtained.

Sample cells for the infrared instrument were composed of two carefully polished rock salt plates held apart a known amount by spacers rolled from aluminum. The thickness of the sample in the beam (length of the optical path through the sample) could be measured with about 5 per cent accuracy. It proved unnecessary to know the thickness to a greater accuracy because of other sources of experimental error of at least that magnitude; both chemical and spectral analysis contributed to these errors. By making certain that the plates and spacer were oriented in the same fashion with respect to each other for each run, conditions throughout an oxidation period could be maintained reasonably constant.

Beer's Law, relating incident and exit electromagnetic radiation intensities to the thickness and absorption properties

of absorbing materials, was first found to hold in the infrared region of the electromagnetic spectrum by Lindholm in 1911 (18). Subsequent work has indicated that it is not always applicable. In the present case it was observed to hold to a fair approximation. Beer's law is stated as follows:

$$I = I_0 e^{-kct}$$

where I_0 is the incident intensity of radiation, I is the exit intensity after passage through the sample, e the base of natural logarithms, k the extinction coefficient characteristic of a given material and a function of wavelength, c is the concentration of the absorbing agent (in this case the concentration or number of the particular functional groups causing the absorption) and t the thickness of the sample through which the radiation passes. By taking the logarithm of both sides of the above relationship and inverting the equation may be restated

$$\log. I_0/I = kct$$

For infrared work the left member, $\log. I_0/I$ is defined as the optical density, OD. It is seen that if Beer's Law is valid this quantity is a linear function of the concentration, c , in any given region (in which k is constant) if the cell thickness is maintained constant.

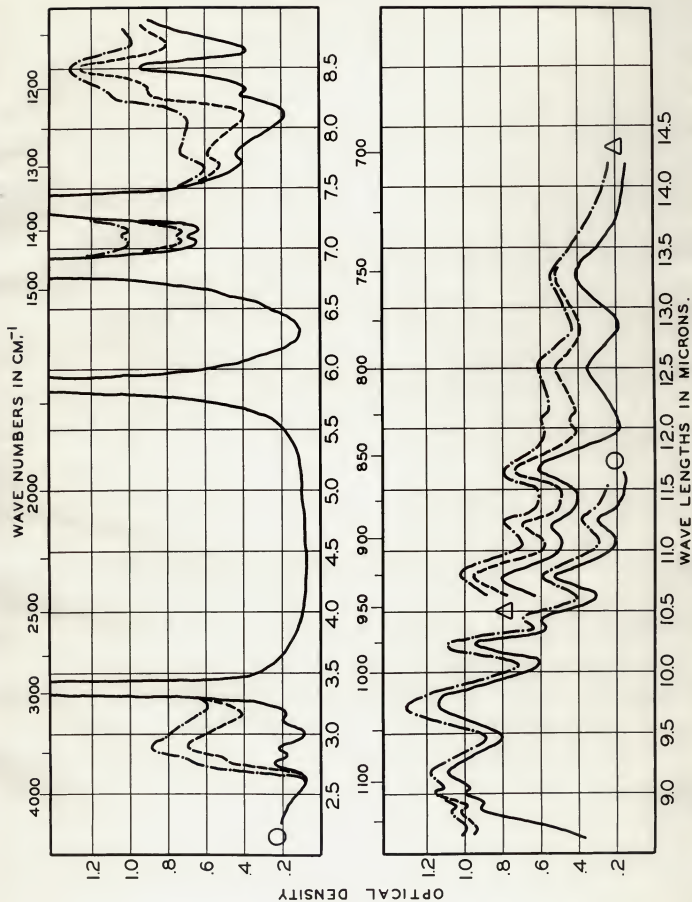
In the analysis of the infrared spectra of di-iso-propyl ketone taken during the period of an oxidation, it was assumed that the concentration of the reaction products in the starting material was zero. Any observed change in the spectrum of the samples during oxidation was then necessarily due to the presence of one or several of the breakdown products. This might be restated by saying that the change in optical density in any

given region of the spectrum was necessarily due to the creation or destruction of some functional group or groups having characteristic absorption in this region. Plate IV is a plot of the spectrum of di-iso-propyl ketone showing the changes which occurred after 16 hours and 26 hours of oxidation; the solid line plot is the spectrum of the pure ketone before oxidation.

For the purpose of calculating the concentrations of the oxidation products, three regions where significant changes occurred were selected. The requirements for these regions were: relatively large changes in optical density during oxidation and relatively small optical density in the spectrum of the pure compound. On this basis the three regions selected were: 2.9-3.1 microns (O-H stretching vibration), 8.0-9.0 microns (skeletal vibrations) and 11.5-13 microns (C-OOH stretching and skeletal vibrations). The assignment of the OH band was made from the catalog of Randall et al. (15). It was not possible to identify the 8.0-9.0 micron region with any specific functional group, thus it was designated only as due to skeletal vibrations. These vibrations are probably vibrations of the carbon atom frame of the molecule or of the molecule as a whole. The assignment of C-OOH stretching vibration to the 12 micron absorption region was made by assuming that the carbon-oxygen binding force is the same in this group as in the C-OH and that, in both cases, the stretching vibration of this bond is due to the motion of the group as a unit vibrating against the adjacent carbon atom whose position is fixed. The difference in frequency in the two cases then is due solely to the difference in mass.

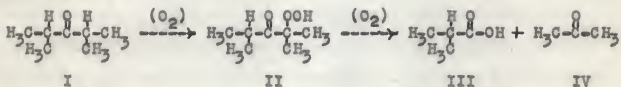
EXPLANATION OF PLATE IV

Infrared spectrum of di-iso-propyl ketone showing
changes due to oxidation. Cell thickness: (O=====O)
0.1 mm ; (Δ ===== Δ) 0.2 mm. Oxidation time:
(=====) 0 hours, pure ketone; (-----)
16 hours; (-----) 26 hours.



Simple calculations (21) show that, on the basis of the assumptions stated, the frequency for C-OOH should be less than that for C-OH by a factor of 0.717. Randall et al. (15) give the C-OH frequency as lying in the range between 1029 and 1282 cm^{-1} . Thus the C-OOH frequency should lie between 738 and 920 cm^{-1} (11.0 to 13.5 microns).

The postulated course of the oxidation of di-iso-propyl ketone was as follows:



where I is the parent ketone, II the hydroperoxide of the ketone, III iso-butyric acid and IV acetone.

For the purpose of determining what changes were produced by each of the reaction products in the three regions selected for quantitative measurements, solutions of the individual products in di-iso-propyl ketone were prepared. These solutions were prepared in several different concentrations for the purpose of determining the extinction coefficients of each product in the regions in question. Solutions were prepared in the following concentrations (in units of millimoles per gram of sample):

Di- <u>iso</u> -propyl ketone	
hydroperoxide	0.739, 0.535, 0.388, 0.196
<u>Iso</u> -butyric acid	0.820, 0.554, 0.353, 0.173
Acetone	0.290, 0.267, 0.127

The changes produced by each component in each of the three

regions are indicated in Figs. 5B, 6B and 7B. From these changes it is to be noted that the change in optical density in each selected region of the spectrum of di-iso-propyl ketone is due to an increase in the concentration of each of the reaction products with the exception of acetone in the 3 micron region. Here acetone exhibits no significant absorption. The change in the spectrum of the ketone upon oxidation is shown in Figs. 5A, 6A and 7A for comparison.

At a particular wavelength where the absorption is due to more than one absorbing group, Beer's Law may be stated:

$$OD_i = (k_{1i}c_1 + k_{2i}c_2 + k_{3i}c_3 + k_{ni}c_n + \dots)t$$

where OD_i is the change in optical density at some particular wavelength designated as i , k_{ni} is the extinction coefficient of the n^{th} absorbing agent at wavelength i , c_n is the concentration of the n^{th} product and t the thickness of the absorbing sample. The solution of this relationship for a particular sample first requires the independent determination of each of the extinction coefficients. In the analysis of the oxidized di-iso-propyl ketone samples, it was required to calculate the concentrations of three products. Thus, it was necessary to know the change in optical density at three particular wavelengths in order to set up three simultaneous equations to be solved. As stated before, acetone had insignificant absorption in the 3 micron region so only two equations were required here; i.e., only the concentrations of di-iso-propyl ketone hydroperoxide and iso-butyric acid could be computed in this region. The extinction coefficients for each of the products were determined at three wavelengths in each of the 8 and 12 micron regions and at two

EXPLANATION OF PLATE V

Fig. 5A Change in optical density in the 3 micron region due to oxidation of di-iso-propyl ketone. Cell thickness 0.1 mm. Prism, lithium flouride. Oxidized: 10 hours (————); 16 hours (-----); 26 hours (-.-.-.-.-).

Fig. 5B Change in optical density in the 3 micron region due to the presence of pure oxidation products. Cell thickness 0.1 mm. Di-iso-propyl ketone hydroperoxide, 0.270 millimoles/g. (-----); iso-butyric acid, 0.353 millimoles/g. (————).

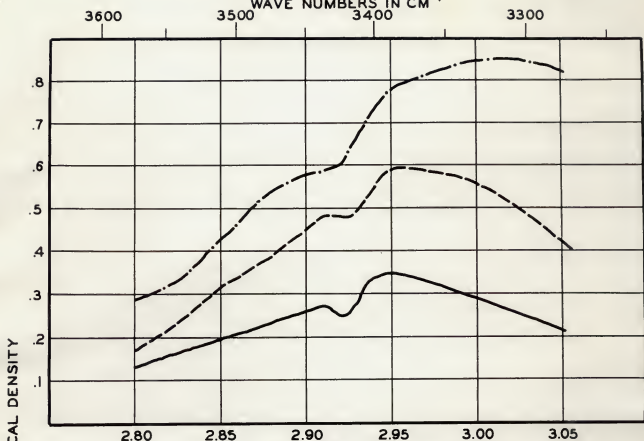


Fig. 5A

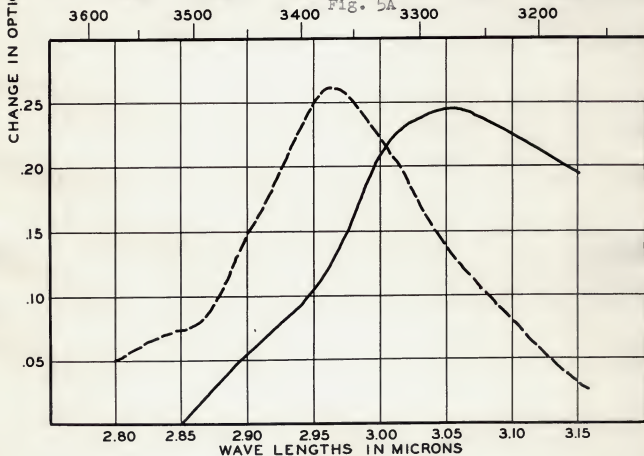
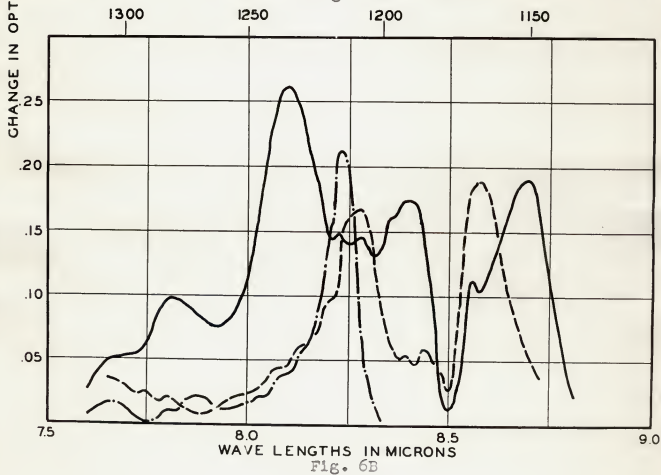
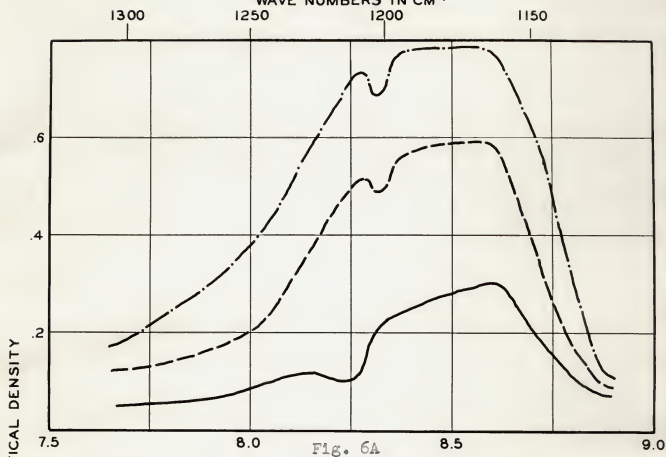


Fig. 5B

EXPLANATION OF PLATE VI

Fig. 6A Change in optical density in the 8 micron region due to oxidation of di-iso-propyl ketone. Prism NaCl. Cell thickness 0.1 mm. Oxidized: 10 hours (————); 16 hours (-----); 26 hours (— · — · — · —).

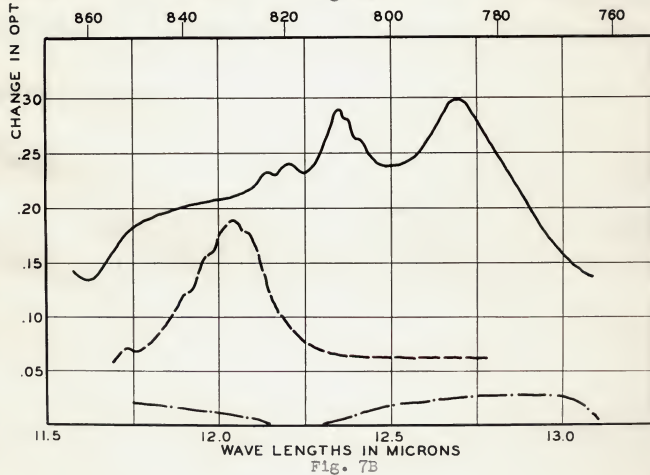
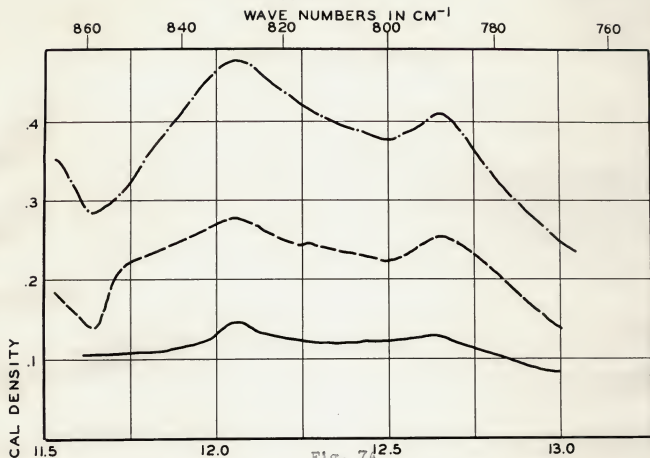
Fig. 6B Change in optical density in the 8 micron region due to the presence of pure oxidation products in di-iso-propyl ketone. Prism NaCl. Cell thickness 0.1 mm. Di-iso-propyl ketone hydroperoxide, 0.739 millimoles/g. (-----); iso-butyric acid, 0.554 millimoles/g. (————); acetone, 0.290 millimoles/g. (— · — · — · —).



EXPLANATION OF PLATE VII

Fig. 7A Change in optical density in the 12 micron region due to oxidation of di-iso-propyl ketone. Prism NaCl. Cell thickness 0.2 mm. Oxidized: 10 hours (————); 16 hours (-----); 26 hours (— · — · — · —).

Fig. 7B Change in optical density in the 12 micron region due to the presence of pure oxidation products in di-iso-propyl ketone. Prism NaCl. Cell thickness 0.2 mm. Di-iso-propyl ketone hydroperoxide, 0.739 millimoles/g. (-----); iso-butyric acid, 0.554 millimoles/g. (————); acetone, 0.290 millimoles/g. (— · — · — · —).



wavelengths in the 3 micron region (the coefficient for acetone was assumed to be zero here). These coefficients were determined by measuring the change in optical density produced by the several concentrations of each product at the particular wavelengths selected. The change in optical density at each wavelength was plotted against concentration for each concentration of a particular product; the slope of the resulting straight line gave the extinction coefficient multiplied by the thickness t . The extinction coefficients calculated in this manner for this problem are listed in Table 2 along with the particular wavelengths selected for measurement.

Table 2. Extinction coefficients for oxidation products of di-iso-propyl ketone. Change in optical density per millimole per gram per millimeter.

Wave length : <u>iso</u> -butyric : Di- <u>i</u> -pr : Acetone (microns) : acid : ketone : : :hydroperoxide :			
2.960	4.21	9.79	0.00
3.065	7.12	4.80	0.00
8.235	5.72	2.42	9.16
8.270	5.75	2.80	4.77
8.690	6.65	1.24	0.00
12.040	2.22	1.32	0.13
12.355	2.87	0.54	0.11
12.695	3.06	0.47	0.43

$$\text{Extinction coefficient} = \frac{\Delta OD}{ct}$$

The additional data necessary for the calculation of product concentrations were the change in optical density at the eight

selected wavelengths. These data were obtained from the spectra of the samples taken during an oxidation run.

The infrared spectra of unoxidized di-iso-propyl ketone and of the ketone oxidized at 110° C. for 16 and 26 hours are shown in Plate IV. These spectra were obtained using a NaCl prism with sample thicknesses of 0.1 mm from 2.0 microns to 11.5 microns and 0.2 mm from 10.5 microns to 14.5 microns. In addition to the above samples, spectra were taken of samples withdrawn after the following periods of oxidation: 1.5, 3.0, 4.0, 5.0, 6.0, 7.0, 8.0, 10.0, 12.0, 14.0, 18.0, 20.0, 22.0, and 24.0 hours.

A second oxidation run was necessary for obtaining the spectra in the 2 micron to 4 micron region with the lithium fluoride prism. Samples were withdrawn at half hour intervals from zero to 8 hours, at one hour intervals from 9 to 14 hours, at half hour intervals from 15 to 20 hours and at one hour intervals from 21 to 28 hours. The sample thickness in this region was 0.1 mm.

By obtaining the spectra with the lithium fluoride prism it was possible to control experimental conditions of the spectrometer with considerably more precision than was the case in taking spectra with the NaCl prism which was used for scanning the entire spectrum from 2 to 15 microns. Due to the intensity variation with wavelength of the infrared source (closely resembling the distribution of intensity with wavelength of a black body radiator) provision was made in the spectrometer for increasing the slit width automatically as the wavelength of the radiation incident on the thermocouple increases.

The rate at which the slit opens is controlled by a pulling attachment on the wavelength micrometer (driven by an electric motor) which is connected to the slit micrometer by a string. The string is wound around both the pulling attachment and the slit micrometer drum and is of such a length as to make it possible to compensate for intensity variation throughout the entire spectrum. With such an arrangement it was unnecessary to stop the instrument for manual adjustment during a run. This advantage, however, introduced an error which proved troublesome in making concentration calculations. The string-pulley slit drive was, of course, not a positive drive arrangement. Due to the elasticity of the string, it was impossible to reproduce the slit setting at any given wavelength. The maximum variation in slit width was about .002 mm; the effect of this error varied with wavelength due again to the intensity distribution with wavelength of the radiation source. The region in which the effect was greatest was in the short wavelengths which included the 2.9-3.1 micron hydroxyl vibration band. Because of the narrow region covered with the LiF prism, it was unnecessary to use the automatic compensating slit drive. The slit was fixed at the beginning of a sequence of runs and remained fixed throughout the oxidation period. As a result the data taken with the LiF prism were considered to be accurate to at least within 5 per cent.

DISCUSSION

From the theory of autoxidation discussed above (see STATEMENT OF PROBLEM) a number of assumptions may be made concerning the progress of an oxidation reaction. If there is

a catalyzing effect due to the presence of the reaction products, the rate of decomposition of the starting compound in the initial stages should increase, thus, the rate of formation of the hydroperoxide should increase. The concentration increase of the hydroperoxide will, in general, depend on its stability or upon the rate with which it decomposes. When the rate of decomposition reaches the rate of formation then the concentration should become constant. The rate of decomposition probably depends on the catalyzing effect of the final products and, if so, the concentration of hydroperoxide would probably not become constant until the concentration of final products became significant.

If a region of change of the infrared spectrum of di-iso-propyl ketone could have been found which was due only to one of the products then a plot of the change in optical density with time of oxidation would have had the same contour as a plot of concentration against time. The change in each region selected was due in some degree to the presence of each of the products. However, at the particular wavelengths selected in each region, the change was produced more by the presence of one of the products than by the others. The plot of optical density against time, indicated in Figs. 8A, 9A and 10A was assumed to have a contour roughly resembling the contour of the concentration vs. time curve.

The actual concentrations of the three reaction products were calculated by the use of the expanded Beer's Law equation discussed above:

$$\Delta OD_1 = (k_{11}c_1 + k_{21}c_2 + k_{31}c_3)t$$

where the extinction coefficients, k_{ni} , used were those given in Table 2 and the change in optical density OD_1 for each sample at each wave length were those given in Figs. 8A, 9A and 10A. The three sets of data were used to calculate three sets of values for the concentrations for each sample. The calculated concentrations of each component as a function of oxidation time are shown in Fig. 8B for the 3 micron region using the optical densities of Fig. 8A, in Fig. 9B for the 8 micron region using data from Fig. 9A and in Fig. 10B for the 12 micron region using the data from Fig. 10A. For comparison the concentrations determined chemically are shown on each concentration curve.

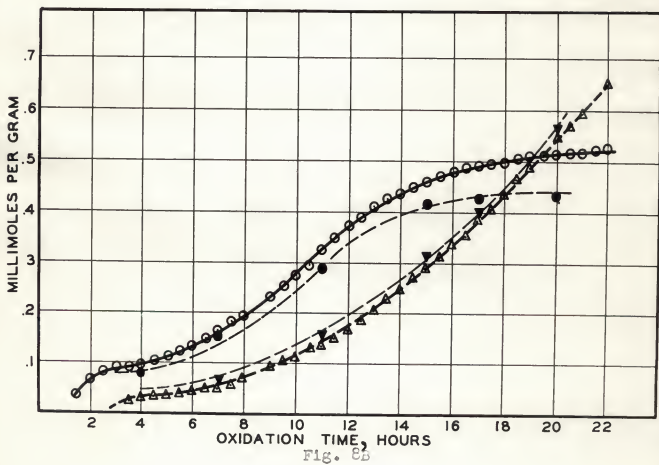
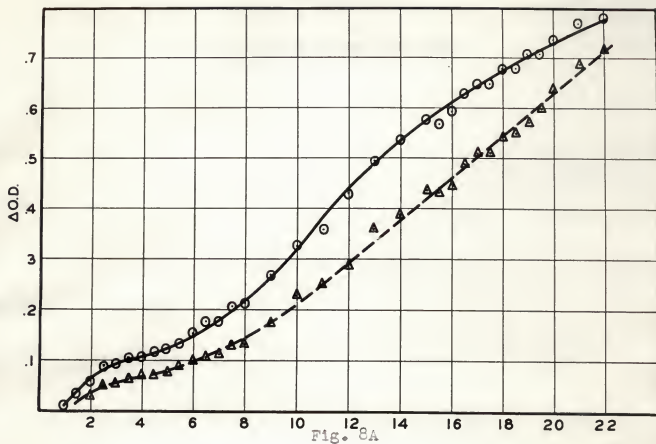
The calculations made from data in the 3 micron region taken with the LiF prism were considered the most accurate. Spectral calculations of acid concentration were very close to the determinations made by chemical analysis. Hydroperoxide concentrations from spectral data were close to chemical determinations up to about 12 hours of oxidation time at which time the spectral data indicated a concentration greater than that determined chemically; the difference reached about 20 per cent at the end point. This difference was greater than the order of the experimental error indicated by the agreement of the acid calculations and thus must have been due to either the presence of an unidentified absorbing agent or to some change in the absorption properties of the hydroperoxide OH group.

Referring to Plate IV, the spectra of di-iso-propyl ketone at three oxidation periods, a conspicuous general increase in absorption occurred from 7.5 to 15 microns. It was not

EXPLANATION OF PLATE VIII

Fig. 8A Change in optical density as a function of oxidation time at 2.96 microns (—○—○—○—) and at 3.065 microns (—△—△—△—).

Fig. 8B Calculated concentrations as a function of oxidation time. Di-iso-propyl ketone hydroperoxide: from 3 micron data (—○—○—○—); from chemical data (—●—●—●—). Iso-butyric acid: from 3 micron data (—△—△—△—); from chemical data (—▼—▼—▼—).



EXPLANATION OF PLATE IX

Fig. 9A Change in optical density as a function of oxidation time: at 6.235 microns ($\square-\square-\square$); at 6.270 microns ($\circ-\circ-\circ$); at 6.690 microns ($\Delta-\Delta-\Delta$).

Fig. 9B Calculated concentrations as a function of oxidation time. Di-iso-propyl ketone hydroperoxide: from 6 micron data ($\circ-\circ-\circ$); from chemical data ($\bullet-\bullet-\bullet$). Iso-butyric acid: from 8 micron data ($\Delta-\Delta-\Delta$); from chemical data ($\nabla-\nabla-\nabla$). Acetone from 8 micron data ($\square-\square-\square$).

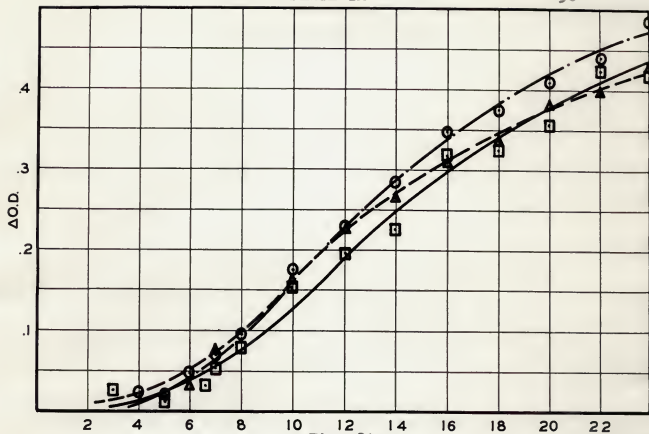


Fig. 9A

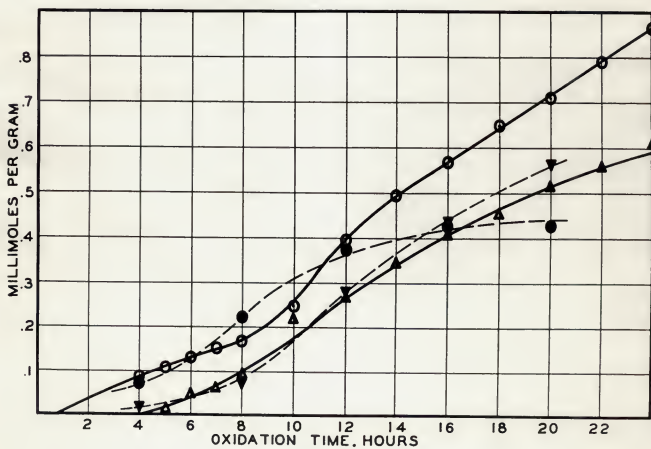
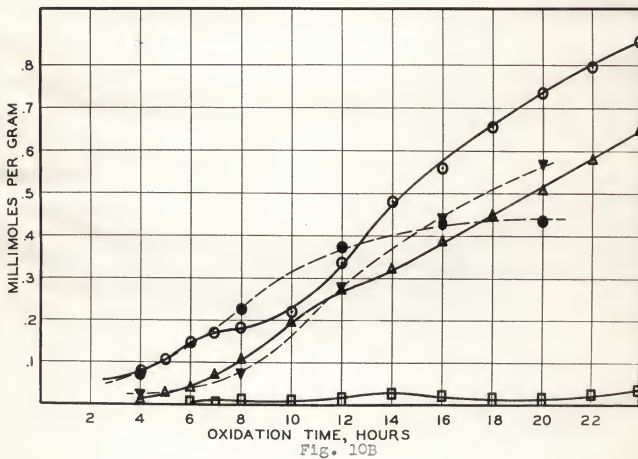
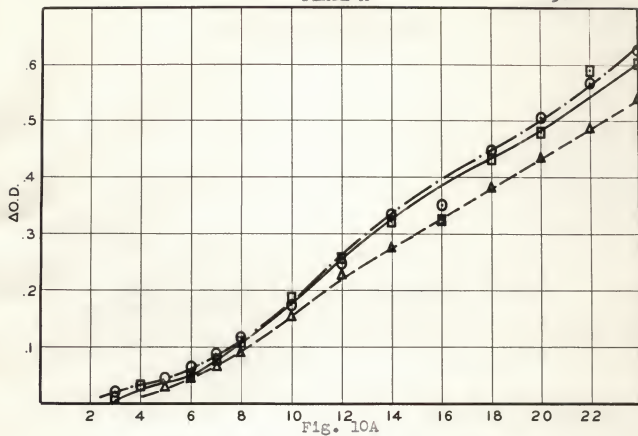


Fig. 9B

EXPLANATION OF PLATE X

Fig. 10A Change in optical density as a function of oxidation time at 12.040 microns ($\circ\text{---}\circ\text{---}\circ$); at 12.355 microns ($\square\text{---}\square\text{---}\square$); at 12.695 microns ($\Delta\text{---}\Delta\text{---}\Delta$).

Fig. 10B Calculated concentrations as a function of oxidation time. Di-iso-propyl ketone hydroperoxide: from 12 micron data ($\circ\text{---}\circ\text{---}\circ$); from chemical data ($\bullet\text{---}\bullet\text{---}\bullet$). Iso-butyric acid: from 12 micron data ($\Delta\text{---}\Delta\text{---}\Delta$); from chemical data ($\nabla\text{---}\nabla\text{---}\nabla$).



believed that experimental error could account for this for two reasons: it occurs in the long wavelength region where a variation in slit width has little effect and because the increase is consistent throughout the entire oxidation period. It was not possible without further experiment to determine the cause of this increase. It resulted in a considerable lack of agreement between chemical and spectral calculations made from the 8 and 12 micron regions of change. In both these regions the acid calculations were in the best agreement; however, the calculations of hydroperoxide concentration were, in both regions, considerably higher than the chemical determined concentrations after 12 hours of oxidation.

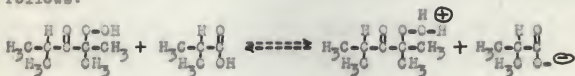
Considerations of the possible experimental errors involved seem to indicate that the discrepancy between the concentrations determined chemically and those determined spectroscopically is real. There is the obvious possibility that an unknown compound was present in the oxidized material which caused the increase in absorption in the 8 and 12 micron regions. However, such a compound would have to have extinction coefficients in these regions which are very similar to those of the hydroperoxide but have zero coefficient in the 3 micron region. It has been assumed that the 12 micron region is due to the absorption of the C-OOH vibration while the 3 micron region is due to the vibration of the O-H. Thus, it seems impossible for one absorbing group to be present without the other, if these assumptions are valid.

Another explanation which seems to have some merit is suggested by a consideration of inter- or intra-molecular

forces which might result in an increase in the intensity of absorption in the 8 micron and 12 micron regions. The hydroperoxide group may form a hydrogen bonded, six membered, chelate ring or it may associate with the carbonyl oxygen of a ketone molecule by hydrogen bonding. Various writers (22, 23) have discussed the effects of these bondings on the infrared spectra of compounds so affected. Each type of bonding is found to produce a shift of the observed frequencies toward lower values and to result in an increased intensity of the band. The range of frequencies attributed to O-H stretching is from 3675 cm^{-1} to 3130 cm^{-1} . This decrease in frequency is in the order of the expected increase in hydrogen bond strength. The O-H stretching frequency of the hydroperoxide was observed at 3378 cm^{-1} (2.96 microns) in solutions of the hydroperoxide in di-iso-propyl ketone. This would indicate the formation of a hydroperoxide-ketone hydrogen bond of intermediate strength. The corresponding acid O-H stretching frequency, 3250 cm^{-1} (3.06 microns), observed for solutions of iso-butyric acid in di-iso-propyl ketone, indicates the formation of acid-ketone bonds of slightly greater strength. Any shift or intensity change produced by hydrogen bonding is necessarily taken into account, therefore, by the choice of the 2.96 micron and 3.06 micron wavelengths and by the use of the extinction coefficients calculated from solutions of the hydroperoxide and of the acid in di-iso-propyl ketone. Since no shifts in frequencies were observed, in addition to those just mentioned, it is doubtful that the discrepancy can be attributed to any differential effect of hydrogen bonding on the 3 micron, 8 micron and 12

micron absorptions.

Another possible intermolecular action involves the hydroperoxide and the acid molecules. This action may be indicated by Figs. 9B and 10B which show that the spectroscopically measured concentration of hydroperoxide rises above the chemical value only after the acid concentration has reached appreciable proportions. The postulated first step of an acid catalyzed ionic decomposition of di-iso-propyl ketone hydroperoxide is as follows:



If such an equilibrium exists, one would expect an increase in the intensity of the hydroperoxide O-H stretching band (2.96 microns) and a decrease in the intensity of the acid O-H stretching band (3.06 microns). This may account for the difference between the chemically measured concentrations and the values calculated from the 3 micron infrared region, Fig. 8B. The presence of the charge on the OOH_2 group in the hydroperoxide ion would undoubtedly increase the dipole moment of the vibrating group involved in the C-OOH vibration, which gives rise to the 12.04 micron band of the hydroperoxide, and possibly increase the dipole moment of the groups involved in the 8 micron vibration region. This increase in dipole moment would produce an increase in the intensity of these bands and so would result in an increase in the actual extinction coefficients of the hydroperoxide as the concentration of the acid increased. Since the calculations

do not take into account such an increase in extinction coefficients the increased optical density due to this change would be interpreted in the calculations as being due to increases in the only variable used, the concentration. These considerations thus suggest that the observed discrepancy between the chemically determined concentrations and those calculated from data obtained in the 8 micron and 12 micron regions are due to the initial stages of an acid catalyzed decomposition of the hydroperoxide. Such a catalyzing effect is predicted by the autoxidation theory discussed previously.

The above possibilities of explaining the discrepancies experienced in this work are only possibilities and have not been justified. Further work is planned in an attempt to note similar discrepancies in prepared solutions of the products of the oxidation of di-iso-propyl ketone. The possibility of the presence of a compound which was not detected chemically will be further investigated.

The original problem, as stated, was to determine by what method ketones in general and in particular di-iso-propyl ketone reacted with molecular oxygen. One of the questions to be answered was whether or not the oxidation proceeded according to the theory of autoxidation. Admitting the failure to explain all spectral changes which occurred, it may be said that the data collected give definite indication that the di-iso-propyl ketone does oxidize as predicted. If one of the possible explanations of the discrepancies is correct, the phase of the catalyzing effect of the intermediate and final products is indicated by the results of this work. It may also be said

of the results that they do definitely indicate that, with further work on technique, infrared spectral analysis will offer a valuable and rapid means of investigating the oxidation processes of other important compounds of which some of the most important are contained in the general family of the hydrocarbons.

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AN INFRARED STUDY OF THE OXIDATION
OF ORGANIC COMPOUNDS

by

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B. S., Kansas State College
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AN ABSTRACT

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ABSTRACT

The infrared spectra of di-iso-propyl ketone which had been subjected to the action of molecular oxygen at 110°C. for periods up to 26 hours were observed from 2 microns to 15 microns. The changes in these spectra were observed as a function of oxidation time. Frequencies characteristic of the chemically observed products of the oxidation of the ketone (di-iso-propyl ketone hydroperoxide, iso-butyric acid and acetone) were chosen by consideration of the spectra of prepared solutions of these products in the ketone. One of these frequencies, 831 cm^{-1} , for the hydroperoxide was tentatively assigned to the C-OOH stretching vibration. Using extinction coefficients derived from the spectra of prepared solutions, three similar sets of calculations were made for product concentrations in the oxidized samples using data obtained in the 3 micron, 8 micron and 12 micron regions. Each set of calculations led to curves showing the concentration of each product as a function of the oxidation time. The concentrations of iso-butyric acid obtained from all three regions are in good agreement with each other and in fair agreement with chemically determined values. The calculated concentrations of di-iso-propyl ketone hydroperoxide using 8 micron and 12 micron data show pronounced deviations from the chemical values and from values calculated from the 3 micron data. Possible reasons for these deviations are discussed.